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(54) Ferroelectric ceramic material.

(57) Proposed are ferroelectric ceramic materials which are Perovskite solid solutions comprising a solid solution of formula

$Pb_{1-a}M_a (Mg_{1/3} Nb_{2/3})_x Ti_y Zr_z O_3$

wherein M is Ba or Sr, x + y + z is 1, a is from 0 to 0.10, x is from 0.05 to 0.70, y is from 0.25 to 0.50 and z is from 0.05 to 0.70, which solid solution contains either (i) at least one oxide selected from La_2O_3, Bi_2O_3 and Nd_2O_3 as group A oxide and at least one oxide selected from NiO, Fe_2O_3, SnO_2 and Ta_2O_5 as group B oxide, with the proviso that NiO or Fe_2O_3 is necessarily contained, or (ii) MnO_2, at least one said group A oxide and at least one oxide selected from NiO, ZnO, Fe_2O_3, SnO_2 and Ta_2O_5 as group B oxide, with the proviso that NiO, Fe_2O_3 or Ta_2O_5 is necessarily contained. These ferroelectric ceramic materials have a large piezoelectric strain constant d.

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FERROELECTRIC CERAMIC MATERIAL

Field of the Invention

The present invention relates to a ferroelectric ceramic material of Pb $(Mg_{1/3} Nb_{2/3}) O_3$ - $PbTiO_3$ - $PbZrO_3$ series. More particularly, it relates to a ferroelectric ceramic material of Pb $(Mg_{1/3} Nb_{2/3}) O_3$ - $PbTiO_3$ - $PbZrO_3$ series having a large piezoelectric strain constant d and an excellent mechanical quality factor Q_m.

Background of the Invention

Piezoelectric materials comprising ferroelectric ceramic materials have heretofore been used in piezoelectric filters, piezoelectric transducers, ultrasonic oscillators and piezoelectric buzzers. The most typical ferroelectric ceramic materials that have been used in such applications are solid solutions of $PbTiO_3$ - $PbZrO_3$ series. Solid solutions of Pb $(Mg_{1/3} Nb_{2/3}) O_3$ - $PbTiO_3$ - $PbZrO_3$ series (Japanese Patent Publication No. 42-9716) and those further containing $BaTiO_3$, $SrTiO_3$ and/or $CaTiO_3$ are also known as having improved piezoelectric characteristics.

On the other hand, use of piezoelectric ceramic materials as an actuator has also been recently studied. In this case, it is necessary to transform electric energy to mechanical energy by the displacement of the piezoelectric ceramic material itself. Accordingly, piezoelectric ceramic materials having a large piezoelectric strain constant d are desired.

The piezoelectric strain constant d, is related to an electromechanical coupling factor k and a relative dielectric constant ϵ, of a piezoelectric ceramic material,as follows:

$d \propto k \sqrt{\epsilon}$

and therefore, in order that the material has a large piezoelectric strain constant d, it must has a large electromechanical coupling factor k and/or a large relative dielectric constant ϵ.

Further, in applications of piezoelectric ceramic materials as a driving part of an actuator, for example, of an ultrasonic motor, where mechanical resonance of the material is utilized, it is desired that both the piezoelectric strain constant d and the mechanical quality factor Q_m are large. When a piezoelectric ceramic material is used in an ultrasonic motor, if the mechanical quality factor Q_m of the material is small, heat is generated due to high frequency driving involved, frequently leading to undesirable reduction in spontaneous polarization of the material and changes in the piezoelectric strain constant of the material with time. Accordingly, it is essential that the mechanical quality factor Q_m of a piezoelectric ceramic material be large, when the material is to be used in ultrasonic motors.

While the mechanical quality factor Q_m of solid solutions of $PbTiO_3$ - $PbZrO_3$ series or of Pb $(Mg_{1/3} Nb_{2/3}) O_3$ - $PbTiO_3$ - $PbZrO_3$ series can be improved by incorporation of MnO_2 thereinto, there has been a problem in that the piezoelectric strain constant d of the material is drastically decreased as the amount of the MnO_2 added increases. Accordingly, base solid solutions prior to the addition of MnO_2 thereto should preferably have a sufficiently large piezoelectric strain constant d.

While various attempts have heretofore been made to add various oxides to solid solutions of Pb $(Mg_{1/3} Nb_{2/3}) O_3$ -$PbTiO_3$ - $PbZrO_3$ series optionally containing $BaTiO_3$, $SrTiO_3$ and/or $CaTiO_3$ for a purpose of increasing the electromechanical coupling factor k and/or relative dielectric constant ϵ, of the solid solutions, thereby increasing the piezoelectric strain constant d of the materials, the attainable level of the piezoelectric strain constant d has not necessarily been satisfactory.

For example, when a solid solution of Pb $(Mg_{1/3} Nb_{2/3}) O_3$ - $PbTiO_3$ - $PbZrO_3$ series optionally containing $BaTiO_3$, $SrTiO_3$ and/or $CaTiO_3$ is incorporated with NiO, the piezoelectric strain constant d of the material is increased as the amount of NiO added is increased. However, when the amount of NiO added exceeds a certain limit, the piezoelectric strain constant d of the material is rather decreased. This is believed because whereas Ni ions preferentially enter B sites of the Perovskite crystals represented by ABO_3, if the amount of NiO admixed with the Perovskite crystals exceeds the certain limit, ions in A sites of the crystals becomes short and, in consequence, a part of the NiO admixed can no longer enter B sites of the Perovskite crystals.

It has now been found that if Perovskite crystals are incorporated with metal ions which enter A sites of the crystals in addition to metal ions which enter B sites of the crystal, such as Ni ions, ferroelectric ceramic materials having a larger piezoelectric strain constant d are obtained when compared with a case wherein the Perovskite crystals are incorporated with metal ions which enter only B sites. It has also been found that

if the so obtained ferroelectric ceramic solid solutions having a large piezoelectric strain constant d are further incorporated with MnO_2, ferroelectric ceramic materials having large piezoelectric strain constant d and mechanical quality factor Q_m are obtained.

Object of the Invention

The invention is based on the above-mentioned findings, and an object of the invention is to provide ferroelectric ceramic materials having a large piezoelectric strain constant d and an excellent mechanical quality factor Q_m, and in consequence, which are excellent in piezoelectric characteristics and are suitable for use in actuators.

Summary of the Invention

A first ferroelectric ceramic material according to the invention is a Perovskite solid solution comprising a solid solution represented by

$Pb_{1-a}M_a (Mg_{1/3} Nb_{2/3})_x Ti_y Zr_z O_3$

wherein M is Ba or Sr, x + y + z is 1, a is from 0 to 0.10, x is from 0.05 to 0.70, y is from 0.25 to 0.50 and z is from 0.05 to 0.70, containing in said solution at least one oxide selected from the group A noted below and at least one oxide selected from the group B noted below, with the proviso that NiO or Fe2O3 is necessarily contained.

Group A : La_2O_3, Bi_2O_3 and Nd_2O_3;

Group B : NiO, Fe_2O_3, SnO_2 and Ta_2O_5.

The first ferroelectric ceramic material according to the invention in which metal ions of oxides selected from the group A and metal ions of oxides selected from the group B are incorporated in A and B sites of the Perovskite crystals, represented by ABO_3, respectively, has a greatly improved piezoelectric strain constant d when compared with known ferroelectric ceramic materials. Accordingly, the first ferroelectric ceramic material according to the invention exhibits excellent characteristics when used in applications such as an actuator.

The second ferroelectric ceramic material according to the invention is a Perovskite solid solution comprising a solid solution represented by

$Pb_{1-a}M_a (Mg_{1/3} Nb_{2/3})_x Ti_y Zr_z O_3$

wherein M is Ba or Sr, x + y + z is 1, a is from 0 to 0.10, x is from 0.05 to 0.70, y is from 0.25 to 0.50 and z is from 0.05 to 0.70, containing in said solution at least one oxide selected from the group A noted below and at least one oxide selected from the group B noted below, with the proviso that NiO, Fe_2O_3 or Ta_2O_5 is necessarily contained, said solid solution further containing in said, solid solution MnO_2.

Group A : La_2O_3, Bi_2O_3 and Nd_2O_3;

Group B : NiO, ZnO, Fe_2O_3, SnO_2 and Ta_2O_5.

The second ferroelectric ceramic material according to the invention in which metal ions of oxides selected from the group A and metal ions of oxides selected from the group B are incorporated in A and B sites of the Perovskite crystals, respectively, and in which MnO_2 is further incorporated, when compared with known ferroelectric ceramic materials, has an improved piezoelectric strain constant d, while retaining a comparable mechanical quality factor Q_m. Accordingly, the second ferroelectric ceramic material according to the invention exhibits excellent characteristics when used in applications as a driving part of an actuator, such as an ultrasonic motor wherein mechanical resonance of the material is utilized.

Detailed Description of the Invention

The ferroelectric ceramic materials according to the invention will now be described in detail.

The first ferroelectric ceramic material according to the invention is a Perovskite solid solution comprising a solid solution represented by

$Pb_{1-a}M_a (Mg_{1/3} Nb_{2/3})_x Ti_y Zr_z O_3$

wherein M is Ba or Sr, x + y + z is 1,
a is from 0 to 0.10, preferably from 0.01 to 0.07,
x is from 0.05 to 0.70, preferably from 0.10 to 0.60,
y is from 0.25 to 0.50, preferably from 0.30 to 0.45, and

z is from 0.05 to 0.70, preferably from 0.10 to 0.60, containing in said solution at least one oxide selected from the group A noted below and at least one oxide selected from the group B noted below, with the proviso that NiO or Fe_2O_3 is necessarily contained.

Group A : La_2O_3, Bi_2O_3 and Nd_2O_3;

Group B : NiO, Fe_2O_3, SnO_2 and Ta_2O_5.

When the Perovskite crystals constituting the first ferroelectric ceramic material according to the invention are represented by ABO_3, a metal of at least one oxide selected from the group A is present in A sites of the crystals in the form of metal ions as noted below, and a metal of at least one oxide selected from the group B is present in B sites of the crystals in the form of metal ions as noted below, with the proviso that NiO or Fe_2O_3 is necessarily contained.

Group A : (La^{3+}, Bi^{3+} or Nd^{3+})

Group B : (Ni^{2+}, Fe^{3+}, Sn^{4+} or Ta^{5+}).

In the solid solution represented by

$Pb_{1-a}M_a(Mg_{1/3}Nb_{2/3})_xTi_yZr_zO_3$

wherein M is Ba or Sr, metal ions of the group A are present preferably in an amount of from 0.5 to 5.0 atom equivalents based on 100 atom equivalents of the sum of Pb and M present in the solid solution. With such an amount of metal ions of the group A, a particularly improved piezoelectric strain constant d can be achieved. The metal ions of the group B are present in the Perovskite solid solution preferably in such an amount so that the relation :

$0.5 \leq N \leq 5.0$

is met, in which N is a defined by the equation :

$$N = \sum_{j=1}^{j} n_{Bj}\, x_{Bj} / \sum_{i=1}^{i} n_{Ai}\, x_{Ai}$$

wherein n_{Ai} and n_{Bj} are valencies of metal ions of the oxides of groups A and B which are present in the solid solution, respectively, and x_{Ai} and x_{Bj} are atom equivalents of metal ions of the oxides of groups A and B which are present in the solid solution, respectively. With such an amount of metal ions of the group B, a particularly improved piezoelectric strain constant d can be achieved.

The second ferroelectric ceramic material according to the invention is a Perovskite solid solution comprising a solid solution represented by

$Pb_{1-a}M_a(Mg_{1/3}Nb_{2/3})_xTi_yZr_zO_3$

wherein M is Ba or Sr, x + y + z is 1,

a is from 0 to 0.10, preferably from 0.01 to 0.07,

x is from 0.05 to 0.70, preferably from 0.10 to 0.60,

y is from 0.25 to 0.50, preferably from 0.30 to 0.45, and

z is from 0.05 to 0.70, preferably from 0.10 to 0.60,

containing in said solution at least one oxide selected from the group A noted below and at least one oxide selected from the group B noted below, with the proviso that NiO, Fe_2O_3 or Ta_2O_5 is necessarily contained, said solid solution further containing in said solution MnO_2.

Group A : La_2O_3, Bi_2O_3 and Nd_2O_3;

Group B : NiO, ZnO, Fe_2O_3, SnO_2 and Ta_2O_5.

When the Perovskite crystals constituting the second ferroelectric ceramic material according to the invention are represented by ABO_3, a metal of at least one oxide selected from the group A is present in A sites of the crystals in the form of metal ions as noted below, and a metal of at least one oxide selected from the group B is present in B sites of the crystals in the form of metal ions as noted below, with the proviso that NiO, Fe_2O_3 or Ta_2O_5 is necessarily contained.

Group A : (La^{3+}, Bi^{3+} or Nd^{3+}); and

Group B : (Ni^{2+}, Zn^{2+}, Fe^{3+}, Sn^{4+} or Ta^{5+}).

In the solid solution represented by

$Pb_{1-a}M_a(Mg_{1/3}Nb_{2/3})_xTi_yZr_zO_3$

wherein M is Ba or Sr, metal ions of the group A are present preferably in an amount of from 0.5 to 5.0 atom equivalents based on 100 atom equivalents of the sum of Pb and M present in the solid solution. With such an amount of metal ions of the group A, a particularly improved piezoelectric strain constant d can be achieved. The metal ions of the group B are present in the Perovskite solid solution in such an amount so that the relation :

$0.5 \leq N \leq 5.0$
is met, in which N is defined by the equation :

$$N = \sum_{j=1}^{J} n_{Bj} x_{Bj} / \sum_{i=1}^{I} n_{Ai} x_{Ai}$$

wherein n_{Ai} and n_{Bj} are valencies of metal ions of the oxides of groups A and B which are present in the solid solution, respectively, and x_{Ai} and x_{Bj} are atom equivalents of metal ions of the oxides of groups A and B which are present in the solid solution, respectively. With such an amount of metal ions of the group B, a particularly improved piezoelectric strain constant d can be achieved.

The amount of MnO_2 contained in solution in the second ferroelectric ceramic material according to the invention is preferably from 0.1 to 2.0 % by weight. With such an amount of MnO_2 contained, an improved mechanical quality factor Q_m can be achieved, while retaining the piezoelectric strain constant d at a satisfactorily high level.

The ferroelectric ceramic materials according to the invention can be prepared by admixing of particulate metal compounds such as oxides and salts in such proportions which provide a desired composition when calcined, and calcining the admixture. Processes for preparing the starting particulate metal compounds are not particularly limited. They may be prepared by various known processes, including liquid phase processes such as precipitation, coprecipitation, alkoxide and sol-gel processes, and solid phase processes such as those based on decomposition of oxalates and blending of oxides. The admixture of particulate metal compounds in appropriate proportions may be pre-calcined at a temperature of from 800 to 1000 °C., pulverized in a ball mill, dried, pressed to a sheet under a pressure of from 500 to 1500 kg/cm^2, and finally calcined at a temperature of from 1000 to 1300 °C., whereupon a desired ferroelectric ceramic material may be obtained.

Examples

While the invention will now be described by the following examples, it should be appreciated that the invention is in no way restricted to the examples.

The radial electromechanical coupling factor Kp, relative dielectric constant ϵ, piezoelectric strain constant d_{31}, and mechanical quality factor Qm of ferroelectric ceramic materials were measured in accordance with Japan Electronic Material Manufactures Association Standard (EMAS).

Examples 1 to 6, and Comparative Examples 1 and 2

PbO, ZrO_2, TiO_2, $MgCO_3$, Nb_2O_5, $SrCO_3$, La_2O_3, NiO and SnO_2 were weighed in proportions which provide each composition as indicated in Table 1, pulverized and admixed in a ball mill. The pulverized admixture was pre-calcined at a temperature of from 800 to 1000 °C. for a period of from 1 to 2 hours, pulverized in a ball mill and dried. The mixture was then pressed to a disc having a diameter of 25 mm under a pressure of about 1000 kg/cm^{2}and finally calcined at a temperature of from 1050 to 1250 °C. for a period of from 1 to 2 hours.

The calcined disc so prepared was polished to a thickness of 0.5 mm, coated with silver paste on both surfaces and baked. It was then polarized by application of a DC electric field of from 20 to 40 KV/cm in a silicone oil and thereafter aged for 12 hours. The specimen so prepared was tested for various electric properties.

The results are shown in Table 1. In Table 1, a, x, y and z represent coefficients appearing in the formula :
$Pb_{1-a}Sr_a (Mg_{1/3} Nb_{2/3})_x Ti_y Zr_z O_3$ [x + y + Z = 1],
p, q and r represent atom equivalents of respective metal ions indicated in the same table based on 100 atom equivalents of the sum of Pb and Sr, and N is a value defined by the equation :

$$N = \sum_{j=1}^{J} n_{Bj}\, x_{Bj} / \sum_{i=1}^{i} n_{Ai}\, x_{Ai}$$

wherein n_{Ai} and n_{Bj} are valencies of metal ions of the groups A and B, respectively, and x_{Ai} and x_{Bj} are atom equivalents of metal ions of the groups A and B, respectively.

Table 1

	Composition							Electric Properties			
	a	x	y	z	Group A Metal Ion	Group B Metal Ion		N	ϵ	Kp	d_{31}
					p	q	r			%	$X10^{-12}$m/V
Example 1	0.05	0.375	0.375	0.250	La^{3+} 2.0	Ni^{2+} 2.0	Sn^{4+} 2.0	2.0	6640	64	376
Example 2	0.05	0.375	0.375	0.250	La^{3+} 2.0	Ni^{2+} 2.0	—	0.67	6220	57	298
Example 3	0.05	0.375	0.375	0.250	La^{3+} 1.0	Ni^{2+} 1.0	Sn^{4+} 1.0	2.0	5960	65	351
Example 4	0.05	0.375	0.375	0.250	La^{3+} 1.0	Ni^{2+} 0.5	Sn^{4+} 1.0	1.67	5060	67	336
Example 5	0.05	0.375	0.375	0.250	La^{3+} 1.0	Ni^{2+} 2.0	Sn^{4+} 2.0	4.0	4430	66	303
Example 6	0.05	0.375	0.375	0.250	La^{3+} 0.5	Ni^{2+} 0.5	Sn^{4+} 0.5	2.0	4530	64	300
Comp.Ex 1	0.05	0.375	0.375	0.250	—	—	—	—	4100	61	267
Comp.Ex 2	0.05	0.375	0.375	0.250	—	Ni^{2+} 2.0	—	—	4460	61	277

It is revealed from Table 1 that when compared with the ferroelectric ceramic material [I] of Comparative Example 1 having a composition of the formula :

$Pb_{0.95}Sr_{0.05}(Mg_{1/3}Nb_{2/3})_{0.375}Ti_{0.375}Zr_{0.250}O_3$

and with the ferroelectric ceramic material of Comparative Example 2 comprising the ferroelectric ceramic material [I] having incorporated with only Ni^{2+} in the B sites, the ferroelectric ceramic materials of Examples 1 to 6 according to the invention, which comprise the ferroelectric ceramic material [I] having incorporated with La^{3+} in the A sites and with Ni^{2+}, or Ni^{2+} and Sn^{4+} in the B sites, do have a larger piezoelectric strain constant d_{31}.

Examples 7 to 14

PbO, ZrO_2, TiO_2, $MgCO_3$, Nb_2O_5, $SrCO_3$, at least one oxide selected from the group A consisting of La_2O_3, Bi_2O_3 and Nd_2O_3, and at least one oxide selected from the group B consisting of NiO, Fe_2O_3, SnO_2 and Ta_2O_5, were weighed in proportions which provide each composition as indicated in Table 2, pulverized and admixed in a ball mill. The pulverized admixture was processed as in Example 1 to prepare a ferroelectric ceramic material, which was tested for electric properties.

The results are shown in Table 2.

Table 2

	Composition							Electric Properties			
	a	x	y	z	Group A Metal Ion	Group B Metal Ion		N	ϵ	Kp	d_{31}
					p	q	r			%	$X10^{-12}m/V$
Example 7	0.05	0.375	0.375	0.250	La^{3+} 2.0	Ni^{2+} 1.71	Ta^{5+} 1.71	2.0	7300	66	394
Example 8	0.05	0.375	0.375	0.250	La^{3+} 1.0	Ni^{2+} 0.86	Ta^{5+} 0.86	2.0	5630	65	339
Example 9	0.05	0.375	0.375	0.250	Bi^{3+} 2.0	Ni^{2+} 2.0	Sn^{4+} 2.0	2.0	5720	61	313
Example 10	0.05	0.375	0.375	0.250	Bi^{3+} 2.0	Fe^{3+} 1.33	Sn^{4+} 2.0	2.0	5660	62	319
Example 11	0.05	0.375	0.375	0.250	Bi^{3+} 2.0	Ni^{2+} 1.71	Ta^{5+} 1.71	2.0	6170	62	327
Example 12	0.05	0.375	0.375	0.250	Nd^{3+} 2.0	Ni^{2+} 2.0	Sn^{4+} 2.0	2.0	6790	62	346
Example 13	0.05	0.375	0.375	0.250	Nd^{3+} 1.0	Ni^{2+} 1.0	Sn^{4+} 1.0	2.0	5800	62	327
Example 14	0.05	0.375	0.375	0.250	Nd^{3+} 2.0	Ni^{2+} 1.71	Ta^{5+} 1.71	2.0	6400	57	296

Table 2 also reveals that joint inclusion of metal ions of the groups A and B into the ferroelectric ceramic material [I] improved the piezoelectric strain constant d_{31}.

Examples 15 to 17, and Comparative Examples 3 to 5

Each of the ferroelectric ceramic materials of the formula :
$Pb_{1-a}Sr_a (Mg_{1/3} Nb_{2/3})_x Ti_y Zr_z O_3$ [x + y + Z = 1],
wherein the coefficients a, x, y and z are different from those of the ferroelectric ceramic material used in Examples 1 to 14, as indicated in Table 3, with (Examples 15 to 17) or without (Comparative Examples 3 to 5) La^{3+}, Ni^{2+} and Sn^{4+} in amounts indicated in Table 3 incorporated therein, was prepared and tested for electric properties in the manner as described in Example 1.

The results are shown in Table 3.

Examples 18 and Comparative Example 6

Ferroelectric ceramic materials were prepared and tested in the same manner as described in Example 1 and Comparative Example 1, except that the $SrCO_3$ was replaced with the equimolar amount of $BaCO_3$.

The results are shown in Table 3.

Table 3

	Composition							Electric Properties			
	a	x	y	z	Group A Metal Ion	Group B Metal Ion		N	ϵ	Kp	d_{31}
					p	q	r			%	$X10^{-12}m/V$
Example 15	0.05	0.500	0.370	0.130	La^{3+} 2.0	Ni^{2+} 2.0	Sn^{4+} 2.0	2.0	6800	60	346
Comp.Ex 3	0.05	0.500	0.370	0.130	—	—	—	—	4690	56	262
Example 16	0.05	0.130	0.430	0.440	La^{3+} 2.0	Ni^{2+} 2.0	Sn^{4+} 2.0	2.0	6220	62	340
Comp.Ex 4	0.05	0.130	0.430	0.440	—	—	—	—	3870	59	250
Example 17	0.03	0.375	0.375	0.250	La^{3+} 3.0	Ni^{2+} 1.5	Sn^{4+} 3.0	1.67	5930	63	341
Comp.Ex 5	0.03	0.375	0.375	0.250	—	—	—	—	3480	59	240
Example 18	0.05	0.375	0.375	0.250	La^{3+} 2.0	Ni^{2+} 2.0	Sn^{4+} 2.0	2.0	6410	64	353
Comp.Ex 6	0.05	0.375	0.375	0.250	—	—	—	—	3830	62	259

Examples 19 to 21, and Comparative Examples 7 and 8

PbO, ZrO_2, TiO_2, $MgCO_3$, Nb_2O_5, $SrCO_3$, La_2O_3, NiO, SnO_2 and MnO_2 were weighed in proportions which provide each composition as indicated in Table 4, pulverized and admixed in a ball mill. The pulverized admixture was processed as in Example 1 to prepare a ferroelectric ceramic material, which was tested for various electric properties.

The results are shown in Table 4.

Table 4

	Composition									Electric Properties			
	a	x	y	z	Group A Metal Ion	Group B Metal Ion		N	MnO_2 (wt%)	ϵ	Kp	d_{31}	Qm
					p	q	r				%	$X10^{-12}$m/V	
Example 19	0.05	0.375	0.375	0.250	La^{3+} 2.0	Ni^{2+} 2.0	Sn^{4+} 2.0	2.0	0.2	5380	59	255	660
Example 20	0.05	0.375	0.375	0.250	La^{3+} 2.0	Ni^{2+} 2.0	Sn^{4+} 2.0	2.0	0.5	2920	57	181	1130
Example 21	0.05	0.375	0.375	0.250	La^{3+} 2.0	Ni^{2+} 2.0	Sn^{4+} 2.0	2.0	1.0	1890	53	140	1210
Comp.Ex 7	0.05	0.375	0.375	0.250	—	—	—	—	0.5	1740	53	129	970
Comp.Ex 8	0.05	0.375	0.375	0.250	—	Ni^{2+} 2.0	—	—	0.5	1800	52	130	1010

Table 4 reveals that in the ferroelectric ceramic material [I] having a composition of the formula : $Pb_{0.95}Sr_{0.05}(Mg_{1/3}Nb_{2/3})_{0.375}Ti_{0.375}Zr_{0.250}O_3$ having incorporated with La^{3+} in the A sites and with Ni^{2+} and Sn^{4+} in the B sites, as the amount of MnO_2 incorporated is increased, the mechanical quality factor Q_m of the material is increased while the piezoelectric strain constant d_{31} of the material is decreased. It has been confirmed, however, that when compared with the ferroelectric ceramic material [I] with or without Ni^{2+}, which enters B sites of the material [I], having incorporated with MnO_2, according to Comparative Examples 7 and 8, the ferroelectric ceramic materials according to the invention whose mechanical quality factor Q_m have been increased to a comparable level of that of the materials of Comparative Examples 7 and 8 by addition of MnO_2, still have a larger piezoelectric strain constant d_{31}.

Examples 22 to 24

PbO, ZrO_2, TiO_2, $MgCO_3$, Nb_2O_5, $SrCO_3$, at least one oxide selected from the group A consisting of La_2O_3, Bi_2O_3 and Nd_2O_3, at least one oxide selected from the group B consisting of NiO, ZnO, Fe_2O_3, SnO_2 and Ta_2O_5, with the proviso that NiO, Fe_2O_3 or Ta_2O_5 was necessarily used, and MnO_2 were weighed in proportions which provide each composition as indicated in Table 5, pulverized and admixed in a ball mill. The pulverized admixture was processed as in Example 1 to prepare a ferroelectric ceramic material, which was tested for electric properties.

The results are shown in Table 5.

Table 5

	Composition									Electric Properties			
	a	x	y	z	Group A Metal Ion	Group B Metal Ion		N	MnO_2 (wt%)	ϵ	Kp	d_{31}	Qm
					p	q	r				%	$\times 10^{-12}$ m/V	
Example 22	0.05	0.375	0.375	0.250	La^{3+} 2.0	Ni^{2+} 1.71	Ta^{5+} 1.71	2.0	0.5	3230	55	184	1070
Example 23	0.05	0.375	0.375	0.250	La^{3+} 2.0	Zn^{2+} 1.71	Ta^{5+} 1.71	2.0	0.5	2540	54	163	1140
Example 24	0.05	0.375	0.375	0.250	Bi^{3+} 2.0	Ni^{2+} 1.71	Ta^{5+} 1.71	2.0	0.5	2500	54	164	1100
Example 25	0.05	0.375	0.375	0.250	Bi^{2+} 2.0	Fe^{3+} 1.33	Sn^{4+} 2.0	2.0	0.5	2300	55	157	1030
Example 26	0.05	0.375	0.375	0.250	Bi^{3+} 2.0	Sn^{4+} 1.33	Ta^{5+} 1.33	2.0	0.5	2690	53	161	1190
Example 27	0.05	0.375	0.375	0.250	Nd^{3+} 2.0	Ni^{2+} 2.0	Sn^{4+} 2.0	2.0	0.5	2760	55	177	980
Example 28	0.05	0.375	0.375	0.250	Nd^{2+} 2.0	Zn^{2+} 1.71	Ta^{5+} 1.71	2.0	0.5	2410	52	154	990

It can be confirmed from Table 5 that the ferroelectric ceramic materials [I] having incorporated with metal ions of the groups A and B together with MnO_2 are materials having an increased mechanical quality factor Q_m and a large piezoelectric strain constant d_{31}.

Examples 29 to 31, and Comparative Examples 9 to 11

Each of the ferroelectric ceramic materials of the formula :
$Pb_{1-a}Sr_a (Mg_{1/3} Nb_{2/3})_x Ti_y Zr_z O_3$ [x + y + Z = 1],
wherein the coefficients a, x, y and z are different from those of the ferroelectric ceramic material used in Examples 19 to 28, as indicated in Table 6, with (Examples 29 to 31) or without (Comparative Examples 9 to 11) La^{3+}, Ni^{2+} and Sn^{4+} in amounts indicated in Table 6 incorporated therein and containing 0.5 % by weight of MnO_2, was prepared and tested for electric properties in the manner as described in Example 1.

The results are shown in Table 6.

Example 32 and Comparative Example 12

Ferroelectric ceramic materials were prepared and tested in the same manner as described in Example 20 and Comparative Example 7, except that the $SrCO_3$ was replaced with the equimolar amount of $BaCO_3$.

The results are shown in Table 6.

Table 6

	Composition									Electric Properties			
	a	x	y	z	Group A Metal Ion	Group B Metal Ion		N	MnO_2 (wt%)	ε	Kp	d_{31}	Qm
					p	q	r				%	$X10^{-12}m/V$	
Example 29	0.05	0.500	0.370	0.130	La^{3+} 2.0	Ni^{2+} 2.0	Sn^{4+} 2.0	2.0	0.5	2830	53	169	1230
Comp.Ex 9	0.05	0.500	0.370	0.130	—	—	—	—	0.5	1870	48	121	1180
Example 30	0.05	0.130	0.430	0.440	La^{3+} 2.0	Ni^{2+} 2.0	Sn^{4+} 2.0	2.0	0.5	2320	52	152	1050
Comp.Ex 10	0.05	0.130	0.430	0.440	—	—	—	—	0.5	1540	48	109	930
Example 31	0.03	0.375	0.375	0.250	La^{3+} 3.0	Ni^{2+} 1.5	Sn^{4+} 3.0	1.67	0.5	1980	55	146	970
Comp.Ex 11	0.03	0.375	0.375	0.250	—	—	—	—	0.5	1370	50	110	930
Example 32	0.05	0.375	0.375	0.250	La^{3+} 2.0	Ni^{2+} 2.0	Sn^{4+} 2.0	2.0	0.5	2520	55	167	1270
Comp.Ex 12	0.05	0.375	0.375	0.250	—	—	—	—	0.5	1660	48	119	1010

Claims

1. A ferroelectric ceramic material which is a Perovskite solid solution which comprises a solid solution of formula

$Pb_{1-a}M_a (Mg_{1/3} Nb_{2/3})_x Ti_y Zr_z O_3$

wherein M is Ba or Sr, x + y + z is 1, a is from 0 to 0.10, x is from 0.05 to 0.70, y is from 0.25 to 0.50 and z is from 0.05 to 0.70, which solid solution contains at least one oxide selected from La_2O_3, Bi_2O_3 and Nd_2O_3 as group A oxide and at least one oxide selected from NiO, Fe_2O_3, SnO_2 and Ta_2O_5 as group B oxide, with the proviso that NiO or Fe_2O_3 is necessarily contained.

2. A ceramic material according to claim 1 wherein metal of said group B oxide is present in the form of Ni^{2+}, Fe^{3+}, Sn^{4+} or Ta^{5+} ions.

3. A ferroelectric ceramic material which is a Perovskite solid solution which comprises a solid solution of formula

$Pb_{1-a}M_a (Mg_{1/3} Nb_{2/3})_x Ti_y Zr_z O_3$

wherein M is Ba or Sr, x + y + z is 1, a is from 0 to 0.10, x is from 0.05 to 0.70, y is from 0.25 to 0.50 and z is from 0.05 to 0.70, which solid solution contains MnO_2, at least one oxide selected from La_2O_3, Bi_2O_3 and Nd_2O_3 as group A oxide and at least one oxide selected from NiO, ZnO, Fe_2O_3, SnO_2 and Ta_2O_5 as group B oxide, with the proviso that NiO, Fe_2O_3 or Ta_2O_5 is necessarily contained.

4. A ceramic material according to claim 3 wherein metal of said group B oxide is present in the form of Ni^{2+}, Zn^{2+}, Fe^{3+}, Sn^{4+} or Ta^{5+} ions.

5. A ceramic material according to claim 3 or 4 wherein the amount of MnO_2 present in the solid solution is from 0.1 to 2.0% by weight.

6. A ceramic material according to any one of the preceding claims wherein metal of said group A oxide is present in the form of La^{3+}, Bi^{3+} or Nd^{3+} ions.

7. A ceramic material according to claim 6 wherein the metal ions of the group A oxide are present in an amount of from 0.5 to 5.0 atom equivalents per 100 atom equivalents of the sum of Pb and M present in the Perovskite solid solution.

8. A ceramic material according to any one of the preceding claims wherein the metal ions of the group B oxide are present in such amount that the relation:

$0.5 \leq N \leq 5.0$

is met, in which N is defined by the equation:

$$N = \sum_{j=1}^{j} n_{Bj} x_{Bj} / \sum_{i=1}^{i} n_{Ai} x_{Ai}$$

wherein n_{Ai} and n_{Bj} are the valencies of metal ions of group A and group B oxides, respectively, and x_{Ai} and x_{Bj} are the atom equivalents of metal ions of the group A and group B oxides, respectively.

9. Use of a ferroelectric ceramic material as claimed in any one of the preceding claims as an actuator.

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(54) Ferroelectric ceramic material.

(57) Proposed are ferroelectric ceramic materials which are Perovskite solid solutions comprising a solid solution of formula
$Pb_{1-a}M_a (Mg_{1/3} Nb_{2/3})_x Ti_y Zr_z O_3$
wherein M is Ba or Sr, x + y + z is 1, a is from 0 to 0.10, x is from 0.05 to 0.70, y is from 0.25 to 0.50 and z is from 0.05 to 0.70, which solid solution contains either (i) at least one oxide selected from La_2O_3, Bi_2O_3 and Nd_2O_3 as group A oxide and at least one oxide selected from NiO, Fe_2O_3, SnO_2 and Ta_2O_5 as group B oxide, with the proviso that NiO or Fe_2O_3 is necessarily contained, or (ii) MnO_2, at least one said group A oxide and at least one oxide selected from NiO, ZnO, Fe_2O_3, SnO_2 and Ta_2O_5 as group B oxide, with the proviso that NiO, Fe_2O_3 or Ta_2O_5 is necessarily contained. These ferroelectric ceramic materials have a large piezoelectric strain constant d.

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	US-A-3 956 150 (H. OUCHI et al.) * claim 1 * ---	1	C 04 B 35/49 C 04 B 35/00
A	FR-A-1 604 356 (MATSUSHITA) * claim * -----	1	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 04 B 35/00 H 01 L 41/00

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
BERLIN	24-01-1991	KESTEN W.G.

CATEGORY OF CITED DOCUMENTS

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